



Novel extractants for the recovery of fermentation derived lactic acid

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ABSTRACT

Reactive liquid–liquid extraction is a promising technology for the removal of lactic acid directly from fermentation media. For over five decades, tertiary amines (e.g. trioctyl amine) have been the state-of-the-art extractants for carboxylic acid extraction. However, to make fermentative carboxylic acid production with *in situ* recovery through extraction economically attractive, higher distribution ratios of the acids are required. The aim of this study was to develop extractants with a higher affinity for carboxylic acids than trioctylamine, and in particular for lactic acid. Key properties to achieve this goal are hydrophobicity and acid affinity. A screening study using functionalized silica compounds showed functional groups containing multiple nitrogen-based functionalities and at least one double bond between nitrogen and carbon displayed higher acid affinity than the single tertiary amine functional group as present in trioctylamine. After incorporating these functional groups in extractants the highest distribution coefficients of lactic acid were observed for N,N-didodecylpyridin-4-amine (27, vs 11 for trioctylamine at 25 °C). Back-extraction was demonstrated to be feasible, and is promoted by increasing the temperature and by addition of an anti-solvent such as heptane achieving single stage recoveries up to 80%.

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1. Introduction

Poly(lactic) acid (PLA) is one of the examples of industrially matured bio-based polymers. Production of its monomer, lactic acid, from renewable resources (biomass) has been the subject of extensive research [1–4] and transition of fossil oil based production to fermentative processes is taking place. Bioprocesses have originally been developed for the production of specialty chemicals and pharmaceutical ingredients [5], where the required volumes are relatively small. Shifting fermentative productions to commodity chemicals requires significantly higher productivity, and involves new challenges – both scientifically and economically [1]. In order to compete effectively with traditional production routes, the costs of bio-based lactic acid production need to be minimized. One way of achieving this, is by reducing the costs of recovery and purification, which currently constitute approximately 60% of the total costs [6]. Also, elimination of by-products is desired to increase the attractiveness of the process to industry [1]. During the

fermentation process, the pH in the fermenter needs to be maintained at a relatively high level (pH = 5–7) – as a too low pH leads to a decrease in microorganism productivity, and may result in its death. The relatively high pH value is typically maintained by addition of lime or chalk to neutralize the lactic acid that is formed in the broth. Hence, the traditional product recovery is based on concentration of clarified fermentation liquor and subsequent reacidification with H₂SO₄ to obtain crude lactic acid [7,8]. Unfortunately, in this way also huge amounts of the by-product calcium sulfate are produced. *In situ* removal of lactic acid would address both purification and end-product inhibition issues. Reactive liquid–liquid extraction is a separation method that can be applied *in situ* and has potential to provide a high recovery yield. For a successful implementation, a proper extractant needs to be identified. Over the last 60 years, extensive research on the potential candidates has been conducted [8–11]. Through all these years of research, tertiary amines with alcohols as diluents remained the state-of-the-art extractants, with trioctylamine (TOA) providing the highest distributions [12]. Recently, Martak and Schlosser [13], and Oliveira and co-workers [14] attempted to apply phosphonium based ionic liquids and demonstrated that at low acid concentrations, these ionic liquids are able to provide higher distribution ratios than traditional extractants diluted in alkanes. However, under conditions comparable with the results obtained by Wasewar et al.

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[9,10], the TOA in 1-octanol remains the extractant–diluent combination with the highest distribution of lactic acid.

When reactive liquid–liquid extraction is to be applied in an *in situ* fashion on a continuous fermentation process, it could mean that the extractant is entered into the bioreactor, but alternatively a continuous cycle of fermentation broth through an extraction unit is possible. This last process option offers more operational flexibility, e.g. the possibility to operate the extraction at room temperature, which is desired to increase the distribution. The work here described was aiming at application in an *in situ* extraction process, that may be executed in such manner that it is not necessary to maintain the fermentation temperature in the extraction process, and in which the use of additional chemicals such as acids and bases is intended to be minimized. An important factor that may limit the use of additional chemicals is the lactic acid concentration in the process. Therefore, typical concentrations that are applied here are more comparable with the concentrations as applied recently by Martak and Schlosser [13] and Oliveira and co-workers [14] than with concentrations that are obtained in classical batch fermentors.

In a previous study on lactic acid extraction, several potential extractants having interesting functionalities to extract lactic acid were identified, but their application was hampered because of severe leaching into the aqueous feed phase [12]. Hence, it was concluded that a novel extractant for lactic acid should not only comprise such an interesting functionality (*vide infra*), but should also be sufficiently hydrophobic to avoid leaching. Design and development of the molecules combining these properties involves time-consuming and expensive custom synthesis. Therefore, an alternative approach to investigate on the lactic acid affinity of functionalities, while avoiding the risk of transfer to the raffinate and extensive synthesis, is preferred.

Functionalized silica compounds may be applied for adsorption of lactic acid. By immobilizing the functional groups, leaching of extractant can be ignored, and the focus can be completely directed to the functionality of the potential extractants. Through application of commercially available functionalized silica beads, the amount of laborious and expensive custom synthesis can be

limited. In this paper, the lactic acid affinity of selected functional groups is studied by lactic acid adsorption on functionalized silica compounds. For the functional groups displaying higher affinity towards lactic acid than TOA, extractant design and syntheses steps were undertaken, followed by extraction studies using the custom synthesized extractants.

Since our previous study [12] has confirmed effectiveness of amine extractants in recovery of lactic acid we have concluded that the interaction between acid and extractant is governed by proton transfer to the nitrogen atom. Following from this conclusion, we have decided to include in the testing pool compounds whose functionalities contain single or multiple nitrogen atoms. Hence, the functionalities that were investigated using functionalized silica compounds included tertiary amine (the reference, corresponding with TOA), piperidine, piperazine, pyridine, guanidine and aminopyridine (Table 1).

2. Materials and methods

2.1. Materials

2.1.1. Commercially available materials

All silica functionalized compounds, i.e. SiliaBond®Pyridine (R43030B), SiliaBond®Dimethylamine (R45030B), SiliaBond®Piperazine (R60030B), SiliaBond®Piperidine (R71530B), SiliaBond®DMAP (75530B) and SiliaBond®TBD (R68530) were ordered at Screening Devices. 1-Octanol (ReagentPlus, 99%) was obtained from Sigma Aldrich. Lactic acid crystals were kindly provided by Purac Biochem and LIX-7950 was provided by Cognis. Trioctylamine (TOA, 98%) was purchased at Fluka.

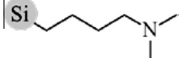
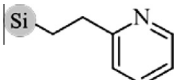
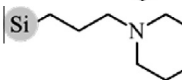
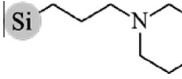
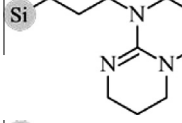
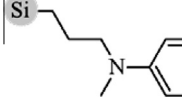
2.2. Methods

2.2.1. Synthesis procedures for the custom synthesized materials

Extractant (2), being 1-(12-((2-hexyldecyl)oxy)dodecyl)-2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2]pyrimidine (95.5%) has

Table 1

Main properties of the functionalized silica compounds used in this study. The hydrogen bond basicity pK_{BHX} , was scaled as described in Laurence and Gal [15], i.e. as the strength of complexation with 4-fluorophenol with carbon π bases in CCl_4 , at 25 °C. 4-Fluorophenol is acidic, and able to form complexes with bases like nitrogen containing compounds. This acid has been applied as a reference complexation agent, and the measured heat of complexation (e.g. using isothermal titration calorimetry) can be used to calculate the complexation constants of the studied bases with 4-fluorophenol. This expression of basicity has been listed in Ref. [15] for many bases, including those in Table 1.

Name silica compound	Silica compound structure	Base used for basicity determination [15]	Hydrogen bond basicity values pK_{BHX} for complexes with 4-fluorophenol with carbon π bases in CCl_4 , at 25 °C ^a	Functional group density (mmol/g)
SiliaBond®Dimethylamine		Diethylamine	1.98	≥ 1.14
SiliaBond®Pyridine		Pyridine	1.86	≥ 0.66
SiliaBond®Piperidine		n-MePiperidine	2.11	≥ 1.03
SiliaBond®Piperazine		Piperazine	2.11	≥ 0.83
SiliaBond®TBD		Guanidine ^a	3.16	≥ 0.83
SiliaBond®DMAP		4-aminopyridine	2.56	≥ 0.53

^a 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, MTBD.

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